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Assessment of olive wastes as energy source: pyrolysis, torrefaction and the key role of H loss in thermal breakdown

Roberto Volpe^a, Antonio Messineo^{a,*}, Marcos Millan^b, Maurizio Volpe^a, Rafael Kandiyoti^b

^a Faculty of Engineering and Architecture, University of Enna "Kore", Cittadella Universitaria, 94100, Italy

^b Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK

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ABSTRACT

The present work describes the first stage of a multi-stage process seeking to develop a usable and cheap design for a downdraft gasifier fed with lingo-cellulosic olive waste. The thermochemical behaviour of two types of olive waste has been assessed during pyrolysis and torrefaction experiments. Olive tree trimmings and olive pulp were pyrolysed in a quartz reactor at peak temperatures between 400 °C and 650 °C, during slow heating experiments (50 °C/min) under a helium blanket. These samples were also torrefied under nitrogen to temperatures between 200 °C and 325 °C. At the peak temperature of 650 °C, mass losses of up to 74% were recorded. Elemental analyses of the chars showed a consistent linear increase of Carbon to values around 75% and a linear decrease of oxygen to values near 10%. By contrast, the H-content remained relatively constant up to about 300 °C and then decreased to as the peak temperature was raised further. The results suggest that the combination of mass loss and H-content may be used as indicators for linear char-GCV increases up to the torrefaction limit of around 300 °C.

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1. Introduction

Residues from agriculture and the agro-industry are a promising source of energy, which is available in large volumes, particularly in rural areas. In inland Sicily, olive cultivation and olive oil production annually generate some 21,000 t/y of olive waste [1], which may be exploited for energy production at local level. The waste is a semi-solid cake with a high moisture content (55–60% wb) and a significant content of polyphenolic compounds, which make it a potentially hazardous material for the environment [2].

Fresh olive pomace from olive mills is traditionally sent to extraction plants where the residual oil (some 4% in weight db) is extracted with the use of solvents. However, the local market for these oils has considerably shrunk in the past years [1]; disposal has thus become an important issue. Vitolo et al. [3] explained how the disposal problem is exacerbated by the diminishing economic attraction of husk oil extraction, compounded by the seasonality of olive oil production, with intense activity during just three months of the year. Moreover, despite the significant pollutant content of

olive wastes, they are commonly spread over open fields [4], posing a hazard to the environment due to the accompanying significant emissions to the atmosphere.

Olive pulp contains significant amounts of proteins, lipids and polysaccharides, but also contains phytotoxic components that inhibit microbial growth [5] and the germination and vegetative growth of plants [6]. As reported in a review of biological treatments for olive pulp [7], olive oil derived phenolic compounds are the main determinants of antimicrobial and phytotoxic actions of olive-mill wastes. Thus, the uncontrolled disposal of olive wastes poses a significant threat for soil and water courses.

The considerable efforts to find optimal mineralization or detoxification procedures for olive wastes through biological methods, have not led to environmentally useful strategies at industrial scale. This appears partly due to the diversity of compounds found in olive wastes, depending on plant variety and the olive oil extraction process. Moreover, as already signalled, many compounds in olive waste are unstable during storage. Current environmental regulations require, therefore, the disposal of olive pulp within maximum 5 days after olive oil extraction [8].

In another work, Chandra and Sathiavelu [9] have proposed composting as "the most efficient means of solving the waste crisis

* Corresponding author. Tel.: +39 0935536448; fax: +39 0935 536951.

E-mail address: antonio.messineo@unikore.it (A. Messineo).

faced by olive oil industries in the Mediterranean region". However, composting of olive waste is not free from drawbacks: Abid and Sayadi [10] had already investigated the detrimental effects of olive mill wastes on the composting of agricultural wastes. The phytotoxicity of olive waste during composting is the main problem and methods are being implemented to control it [11]. Meanwhile, it is noted that despite several attempts to promote the disposal of olive wastes via composting at regional level, there appears to be no market for olive waste derived composts in Sicily [8].

Incineration has been proposed as a solution to the accumulating olive waste problem. However, incineration of fresh olive pomace gives rise to potentially significant emission problems. Jauhiainen et al. [12] pointed out some of the potential hazards related to emissions to the atmosphere during the combustion of olive cake. Whilst they showed how emissions of hydrocarbons can be reduced by adding more oxygen at 800 °C reaction temperature, they observed traces of unburnt material in the ashes in addition to equipment corrosion as well as significant slagging and fouling (ash agglomeration) due to the low melting point of the ashes.

Cliffe and Patumsawad investigated the co-combustion of waste from olive oil production with coal in a fluidised bed reactor [13]. They showed that a 10% olive oil waste concentration gave a lower CO emission than 100% coal firing due to improved combustion in the freeboard region. However, a 20% olive oil waste mixture gave higher CO emissions than both 100% coal firing and coal mixed with 10% olive oil waste. The efficiency of combustion dropped by up to 5%, when coal and pomace were mixed.

More generally, co-combustion does not appear as an attractive proposition for disposing of Sicilian olive wastes, as there are no coal burning power plants in Sicily. Thus the co-combustion option would require the feedstock to be transported over long distances. Added to the seasonality of olive oil production and its high perishability which would oblige some sort of stabilisation prior to transport, co-combustion with coal does not appear as an attractive proposition. It is clear that a 'local solution' would be more advisable. Studies on alternative sustainable uses of the Sicilian agricultural and agro-industrial wastes could significantly foster the development of local waste-fed energy chains, which are still largely lacking [14–16].

One of the most promising alternative to make a virtuous use of the agricultural waste is generating energy by gasification. The money and energy cost of transporting the waste is high relative to the low mass density and low energy density of the feedstock. One attractive solution would involve developing relatively small scale and cheap-to-build downdraft gasifiers, for generating distributed energy sources. The immediate challenges facing the development of this approach are twofold: i) to generate pyrolysis/gasification data on the fundamental behaviour of the samples and ii) to condition the feedstock in order to generally improve the overall energy balance of the process.

The product distributions from the pyrolytic stage of gasification depend on the heating rate, the sample configuration and the reactor configuration as well as the temperature and pressure [17].

With reference to the whole energy balance of the process, the authors have recently attempted a calculation of the net energy available from feedstock after densification [15]. Whilst that study highlighted a positive energy balance from feedstock after densification, it also showed a significant energy consumption especially during the phases of drying and grinding. Therefore, a process able to deliver a uniform product with lower moisture content, higher grindability and higher energy content than raw biomass is desirable.

Torrefaction [18] commonly involves mild heating to 280–300 °C in an inert environment. The solid mass undergoes

some structural and morphological changes and is partially volatilized, leaving behind an easily grindable solid residue with greater energy density [19]. The improvement of biomass characteristics as a solid fuel via torrefaction is widely reported in the literature [20–25]. Sample hygroscopicity [26] and grindability [27] of the feedstock are significantly enhanced while the energy density is increased to values up to 125% of the original energy content [28]. Whilst torrefaction is proved to increase complexity of mechanical pre-treatments of biomass [29], it is considered a valuable pre-treatment route for biomass gasification [30,31].

Recent advances in torrefaction technology and data on several energy crops may be found in a review by Ref. [32].

An interesting study conducted in Brazil [33] on torrefaction of Eucalyptus wood and bark, proposed the use of mass loss as a synthetic indicator for the GCV (gross calorific value) of the torrefied feedstock. That study was conducted on 3 cm wood chips in an oven heated to 250 °C, using a heating rate of 5 °C/min and residence times up to 5 h.

The authors showed a linear correlation between GCV of torrefied feedstock and mass loss. Whilst the correlation demonstrated is certainly of great interest, no explanation was given as to why that correlation exists nor were the limits indicated to which that correlation may hold. One may question whether that correlation is valid for other type feedstock and in different experimental set ups, to what temperature limit is that correlation valid and if that would hold also during pyrolysis for peak temperatures above 300 °C.

In the present study, a further investigation on such correlation serves a stepping stone to more deeply understand the thermal breakdown of biomass and give new insights in such complex phenomenon for which a lot still remains to be explained.

The issue is tackled by using an original integrated approach between mathematical modelling, experimental analysis and SEM (scanning electron microscopy). In order to evaluate the robustness of the model proposed by Refs. [33]; the present study focuses on the behaviour of a different feedstock (pulverised olive tree trimmings and olive pulp as opposed to eucalyptus wood and bark chips) under torrefaction and pyrolysis conditions, in a different set up (horizontal tubular furnace as opposed to ventilated oven), with the broader aim of evaluating the potential utility of these process routes for safe disposal and energy generation.

Experiments were carried out in an inert atmosphere, using a horizontal Gray–King type quartz reactor [34], heated to peak temperatures between 200 and 325 °C with 30 or 45 min holding time during torrefaction experiments, and between 400 and 650 °C with 30 min holding time for pyrolysis tests. The heating rate was 50 °C/min for all experiments. In these experiments, much of the weight loss occurs during heat-up: the final experiment temperature has therefore been consistently referred to as the "peak temperature". The reactor configuration selected for the present work reflects that of a down-draft gasifier (i.e. a fixed bed through which volatiles diffuse) and the heating rates are similar. It is expected that the quality of chars harvested as torrefied product are similar to that of the downdraft gasifier. They can be chemically characterized and their reactivities determined, in order to evaluate the torrefaction procedure.

Similarly, chars collected from pyrolysis at higher temperatures in this reactor would be expected to have similar characteristics to chars generated in the upper section of the downdraft reactor. Once again, these may be chemically characterized and their reactivities determined. The work aims to show that by altering the experimental reactor conditions, this configuration is capable of selecting operating conditions that will be reflected in the design of the downdraft gasifier.

2. Material and methods

2.1. Material selection and sample preparation

Olive trimmings were collected from three 30 years old randomly selected trees of the 'Moresca' variety. The trimmings collected weighted approximately 2 kg and included the leaves. Olive pulp was collected 'as delivered' from a two phase decanter mill located in Enna province. The olives were of the 'Nocellara' variety. The pulp collected was approximately 2 kg in weight (wb) and included the kernels. All samples were dried in an oven at 40 °C for 48 h in order to release excess moisture. The samples were then ground using a rotatory knife mill to particle sizes of <20 mm and milled by a Fritsch "variable speed rotor mill Pulverisette 14" to particle size <2 mm. The milled material was then sieved and the fraction between 425 and 850 µm particle size was selected for the analyses and thermal treatments.

Particles were dried in an oven at 105 °C to remove moisture. The oven dried samples were then exposed to the laboratory ambient atmosphere to reach their EMC (equilibrium moisture content). Prior to each experiment, the sample moisture content was evaluated by thermogravimetric analysis. Moisture content varied typically between 5.9 and 6.3% (wb) for the OT and 6.8–7.5% (wb) for the OP.

ML (Mass loss) after the thermal treatment was calculated according to the formula:

$$\text{Mass loss (ML)} = \left(\frac{M_{\text{sdb}} - M_{\text{tdb}}}{M_{\text{sdb}}} \right) \quad (1)$$

where M_{sdb} represents the sample mass on dry basis before thermal treatment and the M_{tdb} denotes the mass after thermal treatment. "Dry basis" masses were calculated by subtracting the moisture content from the biomass weight ("wet basis").

2.2. Analytical determinations

Ultimate analyses were done using an Elementar Macro Vario Cube analyzer for simultaneous CHNS determination.

Proximate analyses were carried out using a LECO Thermogravimetric Analyser TGA 701. Typically, 200–300 mg of solid samples were used to evaluate composition in terms of MC (moisture content), VF (volatile fraction), FC (fixed carbon) and Ash (ashes). The thermal program was as follows:

- 20 °C/min ramp to 105 °C in air; hold until weight constant ($\pm 0.05\%$) for MC calculation;
- 50 °C/min ramp from 105 °C to 900 °C, hold time 7 min, in N₂ to determine the VF;

- Isothermal hold at 800 °C in a reactive environment (air) to determine the "Ash" content.

Gross (GVC) and net (NCV) calorific values of raw and treated feedstock were evaluated according to the CEN/TS 14918 standard by means of a LECO AC500 calorimeter.

The morphological features and changes undergone by the biomass due to the thermal treatments were evaluated using SEM analysis (FEI Quanta 200 FEG).

2.3. Reaction system set up

The torrefaction and pyrolysis experiments were carried out in a laboratory FBR (fixed bed reactor) adapted from the standard GK (Gray–King) assay test [34].

Fig. 1 shows the general set up and a detail of the reactor used in this work. It consists of a 200 mm long, 30 mm diameter quartz tube equipped with inlet and outlet tubes to allow the carrier gas to flow through the biomass sample while the reaction is running. The biomass sample was held in place by a metal sample holder and two wire meshes in order to minimize the temperature gradient along the sample. A thermocouple placed at the centre of the sample was used to monitor the temperature.

The horizontal quartz reactor was heated by a cylindrical electrical furnace assembled on a mobile cart. With some variations, a similar reactor was recently used for biomass pyrolysis experiments by Cordella et al. (2013) [35].

The reactor was held in place by a metal holder. It was placed inside a cylindrical furnace (Carbolite model MTF12/38/250). The sample was heated to the reaction peak temperature at the controlled heating rate of 50 °C/min. The metal holder was heated up to approximately 180 °C to prevent any condensation in the reactor while a constant flow of 1.5 L/min of N₂ (during torrefaction) or He (during pyrolysis) was used as the inert carrier gas. Condensable material exiting the reactor during the experiment was collected by two successive cold traps: 1) a glass "U" shaped tube immersed in a dry ice/water/ethyleneglycol bath (approx. –27 °C), and 2) a glass finger (30 mm diameter; 180 mm long) placed in a refrigerator (Isotec-6 Venus 2140B) kept at –30 °C. Any uncondensed gas was fluxed through a glass wool filter before it was ducted to the vent through a water bubbler.

2.4. Procedures used during the torrefaction and pyrolysis experiments

Approximately 10 g of sample was weighed to the nearest 0.0001 g and placed in the reactor. In order to measure the moisture content according to CEN/TS 14774 standard, a parallel experiment was carried out with approximately 0.3 g of feedstock placed in a

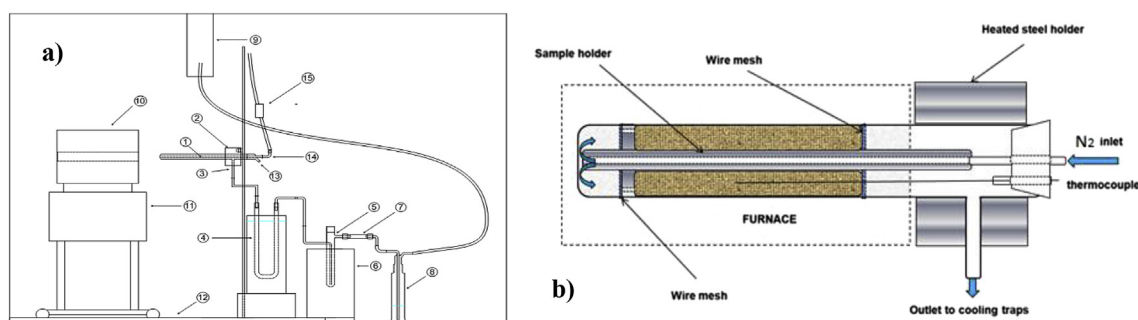


Fig. 1. a) Scheme of the experimental set-up. 1) quartz reactor, 2) heated metal holder, 3) outlet tube, 4) 1st cold trap, 5) 2nd cold trap, 6) isothermal bath (Isotec-6 Venus 2140B), 7) glass wool filter, 8) bubbler, 9) Vent, 10) cylindrical furnace, 11) furnace control panel, 12) furnace tray, 13) thermocouple inlet, 14) inert gas inlet, 15) flow meter. b) Detail of the quartz reactor design.

thermogravimetric balance heated to 105 °C. Wire meshes were weighed to the nearest 0.0001 g for reference in mass balance calculation. The reactor was loaded, assembled and left at room temperature while N₂ (or He for pyrolysis experiments at 400–650 °C) was allowed to flow at 1.5 L/min for approximately 10 min to ensure an inert atmosphere in the system. After reaction peak temperature and heating rates (50 °C/min) were set to desired values, the reactor was heated up to the reaction peak temperature then held at that value for the desired amount of time (30 min or 45 min). Furnace and sample temperatures were recorded by RS-1384 four channel temperature data-logger. Tables 1 and 2 show the set of conditions used during these experiments.

At the end of each reaction, the furnace was slid back and the system was allowed to cool down to room temperature, while N₂ or He was left to flow at the same 1.5 L/min flow rate used during the experiments. When the reactor containing the residual char reached room temperature, the reactor was disassembled; the char and wire meshes were weighed to the nearest 0.0001 g to evaluate mass yields. The tars condensed in the cold traps were collected for mass and energy balance calculations as well as for tar characterization, which will be reported in a subsequent publication.

2.5. Energy properties of chars

The mass yield, energy yield and energy density of the chars were calculated according to the following formulas:

$$\text{Mass yield}(\eta_M) = \left(\frac{M_t}{M_o} \right)_{db} \quad (2)$$

$$\text{Energy yield}(\eta_E) = \eta_M \times \left(\frac{GCV_t}{GCV_o} \right)_{db} \quad (3)$$

$$\text{Energy density}(\eta_D) = \frac{\eta_E}{\eta_M}, \quad (4)$$

where M_t is the weight of char and M_o is the original mass.

2.6. The role of CHO-contents of chars on the GCV values

The role of C, H and O contents of chars on their GCV values was evaluated by combining experimental data with values calculated using the Dulong formula [36] (eq. (5)):

$$GCV = 32.79W_C + 150.40W_H - 13.83W_O + 2.42W_N + 9.26W_S \quad (5)$$

where the W_i is the mass fraction of the element “i”. The Dulong formula shows that GCV increases when carbon, hydrogen, nitrogen and sulphur contents increase and when the oxygen concentration decreases.

Table 1

Torrefaction conditions applied to the biomass in the present study. Biomass type: Olive trimmings and Olive Pulp, atmosphere: N₂.

Torrefaction conditions	
Residence time (min)	Peak temperature (°C)
30	200
	250
	300
	325
45	200
	250
	300

Table 2

Pyrolysis conditions applied to the biomass in the present study. Residence time: 30 min, atmosphere: He.

Sample	Pyrolysis conditions
	Peak temperature (°C)
Olive trimmings	400
	500
	650
Olive pulp	400
	500
	650

N and S play a less important role, as shown by the lower coefficients in the formula, and also because of their usually low concentrations in the feedstock. As will be shown in the results and discussion section, the values remain low for both the torrefied and pyrolysed residues. Thus the GCV largely depends on the C, H and O contents of product phases formed during torrefaction and pyrolysis.

The correlations between C, H, O concentrations vs mass loss were plotted in order to evaluate the influence that each of the elements carries on the GCVs of the solid residues.

3. Results and discussion

3.1. Proximate and ultimate analyses

Table 3 presents proximate and ultimate analysis data for the untreated samples and solid residues after thermal treatment. As expected, the data show “Fixed Carbon” and “Ash” increasing with the severity of thermal treatment, while the solid residue shows diminishing contents of volatile matter. No evidence of significant differences in the solid residues treated at 30 and 45 min holding time was observed for the 200 °C and 250 °C peak temperatures, while a significant decrease of volatiles was found between 30 min and 45 min residence time at 300 °C for both feedstocks. The

Table 3

“Proximate” and “Ultimate” (i.e. elemental) analyses of chars from OT and OP. Analyses were done in duplicates; average values are shown. All values are reported on dry basis. (VM = volatile matter, FC = fixed carbon, Ash = ashes).

Sample	Proximate analysis			Ultimate analysis				
	VM	FC	Ash	C	H	N	S	O
OT raw	75.13%	14.58%	4.06%	49.27%	6.06%	2.09%	0.16%	38.36%
OT 200 °C – 30 min	77.09%	16.54%	4.74%	51.61%	6.19%	1.12%	0.19%	36.15%
OT 200 °C – 45 min	77.65%	16.79%	4.82%	51.70%	6.18%	1.16%	0.19%	35.95%
OT 250 °C – 30 min	72.82%	21.73%	4.69%	56.71%	6.06%	1.48%	0.19%	30.88%
OT 250 °C – 45 min	72.63%	22.23%	3.87%	56.09%	6.06%	1.47%	0.18%	32.33%
OT 300 °C – 30 min	64.34%	29.33%	4.71%	66.71%	5.71%	1.97%	0.23%	20.68%
OT 300 °C – 45 min	61.71%	30.62%	6.82%	66.39%	5.55%	1.07%	0.24%	19.94%
OT 325 °C – 30 min	55.96%	32.57%	7.87%	71.16%	5.48%	2.24%	0.11%	13.15%
OT 400 °C – 30 min	39.12%	48.71%	10.77%	67.98%	4.07%	1.78%	0.17%	15.23%
OT 500 °C – 30 min	28.14%	56.28%	13.41%	70.44%	2.54%	1.58%	0.19%	11.84%
OT 650 °C – 30 min	20.90%	60.16%	14.40%	73.07%	1.36%	1.60%	0.22%	9.35%
OP raw	69.68%	19.78%	3.12%	52.66%	5.92%	2.67%	0.16%	35.47%
OP 200 °C – 30 min	74.70%	21.68%	2.61%	52.54%	6.16%	0.97%	0.10%	37.62%
OP 200 °C – 45 min	77.22%	19.98%	1.50%	53.26%	6.29%	1.05%	0.10%	37.80%
OP 250 °C – 30 min	66.26%	29.19%	2.91%	59.97%	6.07%	1.23%	0.08%	29.73%
OP 250 °C – 45 min	64.43%	30.77%	3.45%	61.60%	6.37%	1.40%	0.09%	27.09%
OP 300 °C – 30 min	49.73%	43.32%	4.52%	68.18%	5.62%	1.49%	0.09%	20.11%
OP 300 °C – 45 min	41.99%	50.40%	5.31%	71.51%	5.10%	1.61%	0.09%	16.39%
OP 325 °C – 30 min	48.91%	43.07%	6.67%	71.23%	5.49%	1.63%	0.09%	16.90%
OP 400 °C – 30 min	33.35%	56.87%	8.77%	70.87%	3.80%	2.26%	0.11%	14.19%
OP 500 °C – 30 min	23.40%	65.12%	11.21%	75.26%	2.68%	2.06%	0.12%	8.66%
OP 650 °C – 30 min	20.87%	67.94%	10.69%	79.59%	1.54%	2.09%	0.13%	5.96%

significance of the residence time appears only at the 300 °C and is not expected as a trend for higher temperatures. In fact, 300 °C is a transition temperature where differences in thermally treated feedstock start to become more important. At temperatures both lower and higher than 300 °C, the greater part of the changes occur during heat-up and the first few minutes of holding at peak temperature.

The ultimate (i.e. elemental) analyses show that carbon content in solid residue (char) increased as reaction conditions become more severe. The H-content remained nearly constant up to 300–325 °C, but decreased rapidly at higher temperatures. Changes in nitrogen and sulphur appear marginal during different thermal treatments, indicating equipartition between the char and evolving volatile matter.

3.2. Energy properties of chars

Fig. 2(a–b) presents changes in mass loss as function of reaction peak temperatures and Fig. 2(c–d) the relationship between mass loss and GCV. The data may be analysed in terms of two distinct zones: 1) a torrefaction zone, conventionally considered up to approximately 300 °C and 2) a pyrolysis zone between 300 °C and 650 °C. The transition was found to occur at approximately 50% mass loss for both OT and OP samples. A linear correlation between peak temperature and mass loss is clearly visible in the torrefaction zone, while for temperatures above 300 °C, or mass losses above 50%, the relationship becomes non-linear. The increase in mass loss is only marginal with increase in holding time from 30 to 45 min at the same temperatures.

The char yields shown in Fig. 2 may be considered as high, compared to reactor configurations where secondary tar deposition could be minimized. However, these experiments have been designed within the context of the intended development of a downdraft gasifier, where there is interaction between chars and

evolving volatiles. The present experimental configuration is therefore deemed as more relevant to the problem at hand.

Fig. 3 shows the energy yields and the energy densities vs mass loss. Data demonstrate how, once again, 50% mass loss represents a turning point from which correlations change while energy yield starts to decrease more rapidly and energy density reaches its higher value. The linear relationships observed in the torrefaction zone are similar to work published by Almeida et al. [33]. However this correlation ceases to be valid for temperatures above 300 °C.

Elemental CHNS analyses of the present samples have shown N-contents between 0.9% and 2.09% and S-contents between 0.09% and 0.2%. As already signalled, changes observed after thermal treatment were relatively minor. The W_S and W_N factors can therefore be neglected in the Dulong formula calculations and the formula may then be rewritten as:

$$GCV = 32.79W_C + 150.40W_H - 13.83W_O \quad (6)$$

Fig. 4 presents GCVs calculated using the Dulong formula, showing that these values were comparable to those arrived at experimentally. Smaller differences were observed between experimental and calculated values in the torrefaction zone.

Fig. 5 presents changes in the C, H and O-contents of the chars as a function of mass loss during the torrefaction and pyrolysis experiments. The C-contents showed a consistent linear increase to values around 75% for 70% mass loss in the case of the more severe thermal treatment at 650 °C. A downward linear trend was shown by oxygen, which decreased linearly to values near 10%, under the more severe experimental conditions.

Hydrogen, on the other hand, showed a remarkably different behaviour as its concentration remained effectively constant for treatment up to 300 °C (torrefaction). It decreased nearly linearly for temperatures above that value (pyrolysis). Similar trends were found for both feedstocks.

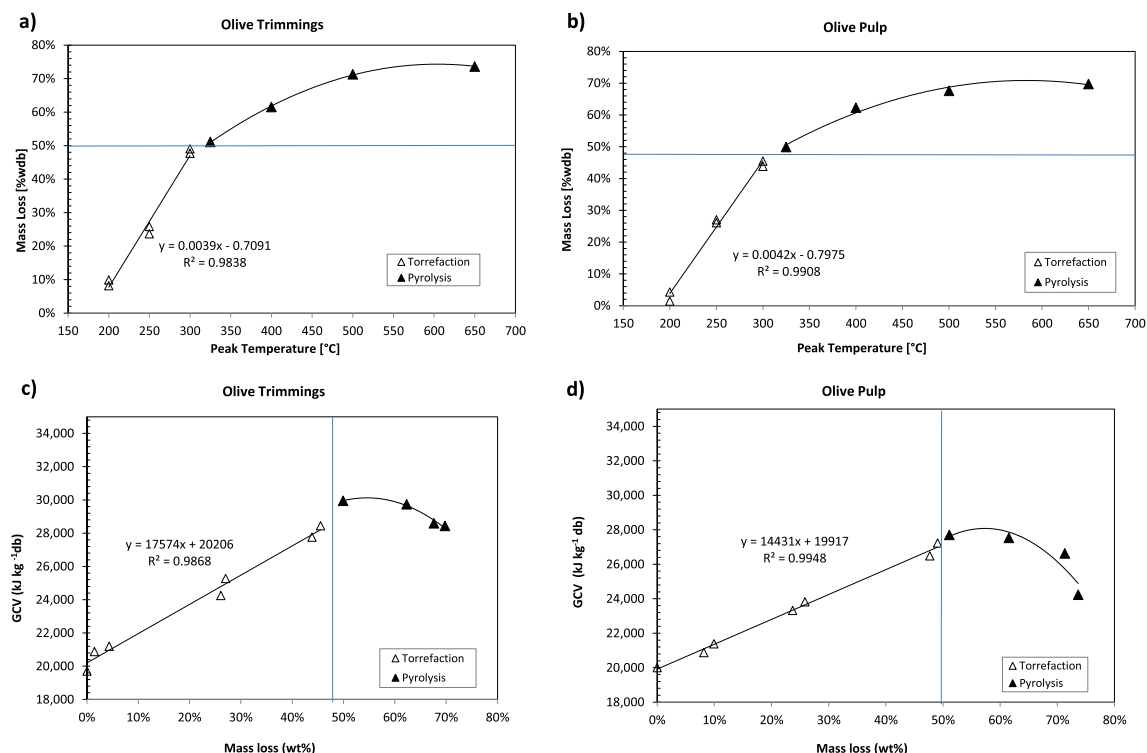


Fig. 2. Correlation between Mass Loss versus thermal treatment Peak Temperature (a, b); Correlation between Mass Loss and GCV (c, d), for both 30 min and 45 min experiments.

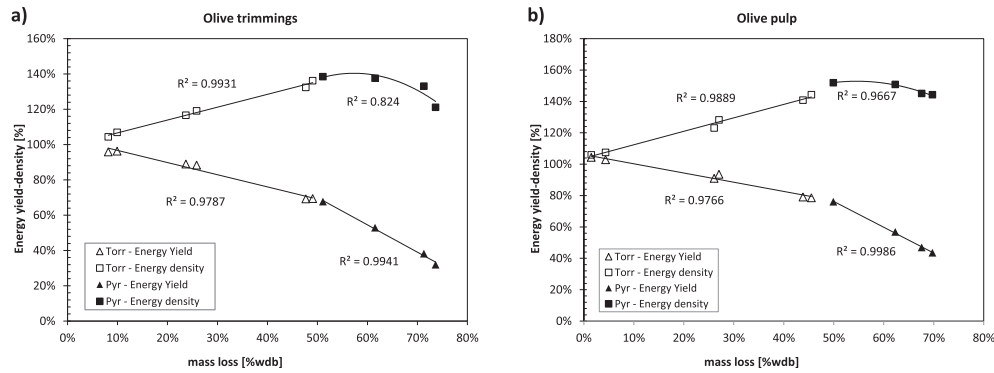


Fig. 3. Energy yield and energy densities of torrefied and pyrolysed chars. OT and OP, conditions as shown on Tables 1 and 2 (30 min and 45 min reaction times).

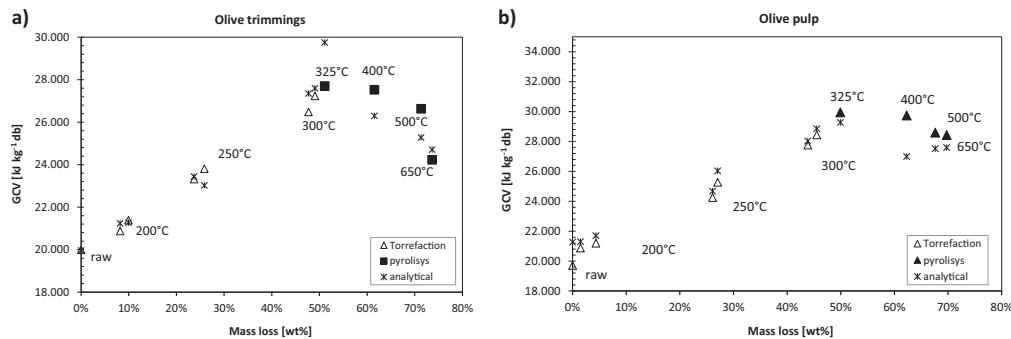


Fig. 4. Variation of Char-GVCs with mass loss (severity of the treatment): comparison between GCVs obtained experimentally and GCVs according Dulong formula. OT and OP, conditions as shown on Tables 1 and 2 (30 min and 45 min reaction times).

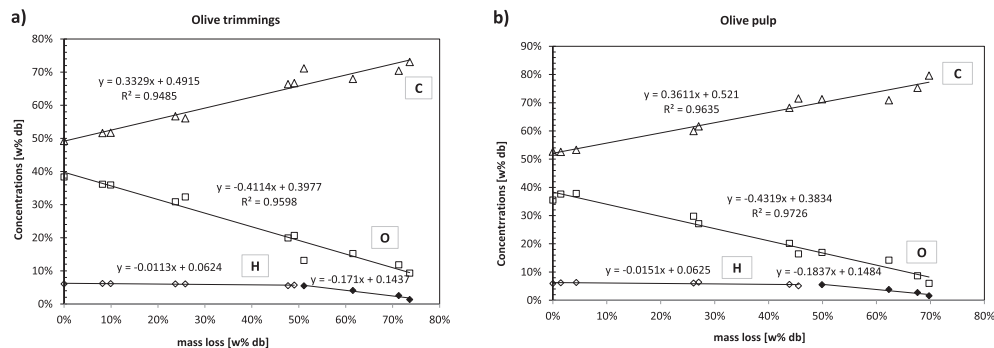


Fig. 5. Variation of C, H, and O elements concentrations with mass loss.

If the analytical formula with the linear trends are combined by multiplying the Dulong element coefficients with the corresponding slopes shown in Fig. 5, the GCV as a function of mass loss can be written as follows:

3.2.1. Torrefaction

Olive trimmings

$$\text{GCV(ML)} = 10.91 \text{ ML}_C + 5.69 \text{ ML}_O - 1.70 \text{ ML}_H + K \quad (7)$$

Olive pulp

$$\text{GCV(ML)} = 11.95 \text{ ML}_C + 6.03 \text{ ML}_O - 2.31 \text{ ML}_H + K \quad (8)$$

3.2.2. Pyrolysis

Olive trimmings

$$\text{GCV(ML)} = 10.91 \text{ ML}_C + 5.69 \text{ ML}_O - 25.72 \text{ ML}_H + K \quad (9)$$

Olive pulp

$$\text{GCV(ML)} = 11.95 \text{ ML}_C + 6.03 \text{ ML}_O - 27.62 \text{ ML}_H + K \quad (10)$$

Where ML_i indicates that the term in the polynomial expression derives from the trend in concentration of element “i” as reported in Fig. 5. Equations (7)–(10) thus show the effect of individual elemental contents on the GCV of the solid products. They indicate

that negligible differences exist in the behaviour of the two feedstocks during torrefaction and pyrolysis. GCV tends to increase due to an increase in C concentration and a decrease in O concentration, while it tends to decrease with a drop in H concentration.

Comparing equations (7) and (8) with equations (9) and (10), it is clear that the change in H concentration shown in Fig. 5 for values above 50% mass loss is responsible for the change of trend and the decrease in GCV shown in Figs. 2 and 4.

In summary, GCVs were observed to increase to a maximum value as the severity of thermal treatment causes mass losses up to 50%. For more severe treatments and mass losses above that value, GCV values decreased, due mainly to the decrease in H concentration, although reactor configuration makes it difficult to distinguish between hydrogen loss through tar release and elemental hydrogen release from solidifying residue. Tar recovering during pyrolysis show that above 300 °C all tars have been released by the samples both for OT and OP. OT samples tar yield remain constant above 300 °C with a value of about 43% db while OP tar mass yield slowly decreases above 300 °C from a value of 42% to a value of 35% db at 650 °C.

The tar mass yield data suggest that hydrogen loss is directly associated with volatile loss and become more and more important at temperature above 300 °C, causing a drop in the GCV of the solid products. Thus, thermal treatments may be used as a 'pre-treatment' to increase the energy content of the solid products only up to approximately 300 °C or 50% mass loss. Peak temperatures above that value cause mass losses over 50%, and a decrease in feedstock energy properties.

The resulting char structures in torrefaction and pyrolysis were investigated by SEM (scanning electron microscopy) in order to further investigate the mass loss phenomenon. Fig. 6 shows SEM images of (a) untreated, (b) torrefied OT (300 °C 45 min holding time) and pyrolysed feedstock (650 °C peak temperature) at 20 µm (c) and 100 µm scale. These images clearly show how the matter is degraded after thermal treatment. Whilst the initial tubular structure appears to be largely preserved even after the more severe 650 °C pyrolysis, the cell walls do not show the typical layered structure after treatment, instead they appear somehow 'coated'. This phenomenon may be linked to some of the tar released from the particles further upstream in the fixed bed reactor depositing on the particles downstream; such deposition is thought to be accompanied by some cracking giving off lighter products and some secondary-char, which tends to 'coat' primary char surfaces.

The 'coating' interpretation seems consistent with the state of the sample pyrolysed at temperatures up to 650 °C, in the larger scale photomicrograph, shown in Fig. 6(d). This image clearly shows a surface that appears to have undergone 'bubbling.' The effect seems consistent with volatiles being released by the deposited tar, which appears to have been still soft when volatiles were being released. The condensed tar 'coating' appears to have been swollen and burst in several localities before hardening into a "secondary char".

This effect appears interesting and would need to be investigated in greater detail, as confirmation of the sequence of events would lead to a more thorough understanding of the manner of tar deposition in fixed bed reactors and the formation of secondary

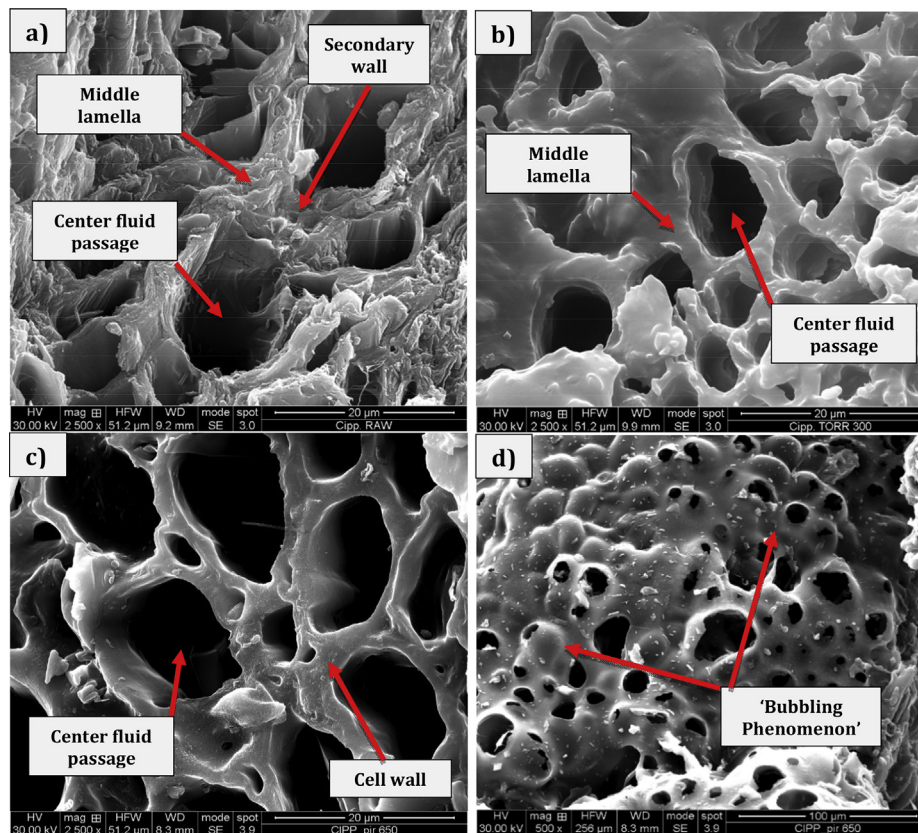


Fig. 6. SEM images of raw olive trimming (a), torrefied at 300 °C peak Temperature (b), pyrolysed at 650 °C peak temperature (c) and the 'bubbling phenomenon' on pyrolysed feedstock at 650 °C (d). The cell structure appears largely preserved after thermal treatment, however a 'melting' or 'coating' phenomenon appears on the treated cell walls. A bubbling phenomenon is observed on the larger scale photogram feedstock at 650 °C peak temperature.

chars, which has in the past been deduced from comparative weight loss experiments in reactors with different configurations [37–39].

4. Conclusions

Olive tree trimmings and olive pulp samples were torrefied under nitrogen by heating to temperatures between 200 °C and 325 °C, and pyrolysed at peak temperatures between 400 °C and 650 °C under a helium blanket in a horizontal tubular quartz reactor. For the two samples, torrefaction experiments at peak temperatures of around 300 °C were observed to give about 50% mass loss while pyrolysis at 650 °C led to mass losses in excess of 70%. These char yields are high compared to reactor configurations where secondary tar deposition can be minimized. However, the present set of experiments has been designed in the context of developing a downdraft gasifier and the present experimental configuration selected was deemed to be more relevant to the problem at hand.

A linear trend was observed between peak temperature and mass loss in torrefaction temperatures up to 300 °C. Mass loss during thermal treatment above that temperature gave rise to a less steep quasi-parabolic curve. At a peak temperature of 650 °C with 30 min holding time, the energy density of the char sample was 140% of the original sample. As the severity of the process was increased up to 300 °C (i.e. in torrefaction zone), carbon-contents of recovered chars were also observed to increase linearly with temperature and mass loss. Over the same experimental range, the oxygen-contents decreased linearly, while the concentration of H remained effectively unchanged up to 300 °C. However, in pyrolysis conditions at temperatures above 300 °C, although the concentrations of C and O maintained the same trends, the H-content decreased nearly linearly and this was accompanied by a marked decrease in GCV. The reported work has therefore shown that the progress of thermochemical processes may be tracked by determining the concentration of residual hydrogen in the biomass chars.

The combination of mass loss and hydrogen content may be used as indicators for linear char-GCV increases up to the torrefaction limit of around 300 °C. The drop in H/C ratio, which occurs at temperatures above 300 °C, suggests a direct link between decreasing H-content and the quasi-parabolic decline in GCV above this temperature. The results indicate that torrefaction may be a valid pre-treatment method for these samples, to increase the energy density of the biomass, up to the point at which H-loss becomes significant above 300 °C.

The accompanying SEM work has revealed the precise stages by which the current biomass samples thermally decompose. The morphological changes are interesting and important in their own right, as well as being technologically relevant to the design of the downdraft reactor.

Chars observed by SEM largely maintained their original morphology. However, a “coating” phenomenon is likely to have originated in the deposition of tars on heated particles, eventually leading to a fine layer of secondary char, which presages the loss of reactivity observed in past work. The condensed tar “coating” appears to have been swollen and burst in several localities before hardening into a “secondary char”. The effect seems consistent with the deposited tar releasing volatiles, which appears to have taken place when the tar layer was still soft.

These observations need to be investigated in greater detail. The confirmation of the sequence of events would lead to a more thorough understanding of the manner of tar deposition in fixed bed reactors and the formation of secondary chars, which has in the past been deduced from comparative weight loss experiments alone, in reactors with different configurations, but never observed directly and with such clarity.

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